2 Analysis of Variations in Ozone & Ozone Precursors

2.3 Analysis of VOC to NO_X Ratios in the South Coast Air Basin

2.3.1 Abstract

This section presents calculated VOC to NO_X ratios for six sites in the South Coast Air Basin. Total non-methane organic carbon (TNMOC) measured for the PAMS program was used for the VOC concentrations. Hourly NO_X values were averaged to allow comparison with three-hour VOC canister samples. The late-morning (8:00 – 11:00) VOC/NO_X ratios are typically 10 to 30% higher on weekends than weekdays with average weekend VOC/NO_X ranging from 5.0 – 9.3 and average weekday ratios ranging from 4.4 – 7.3. However, uncertainties regarding actual VOC concentrations, as well as spatial and temporal variations in the ozone isopleths make it difficult to determine the effect on ozone concentrations of this increase in VOC/NO_X ratio from weekday to weekend.

2.3.2 Introduction

The chemistry involved in tropospheric ozone production non-linear with respect to volatile organic compounds (VOC) and NO_X. The ratio of VOC concentration to NO_X concentration can provide information as to the effect on the ozone concentration of changes in precursor concentrations. If the VOC/NO_X ratio is greater than approximately 8, the system is termed NO_X-limited and decreases in NO_X are expected to decrease ozone. If the VOC/NO_X ratio is less than 8, the system is termed VOC limited and decreases in NO_X are expected to increase the peak ozone concentration. However, simple two-dimensional isopleths, such as shown in Figure 2.3-1, encourage an overly simplistic application of VOC/NO_X ratio to predict behavior. Three-dimensional isopleths (see for example pages 883-885 in Finlayson-Pitts, 2000) provide a more complete picture of how changes in precursor concentrations affect ozone concentrations. In addition to VOC and NO_X concentrations, factors that influence the shape of the isopleth include composition of the VOC and NO_X mixtures, both of which will change over time. Thus, while the VOC/NO_X ratio is a key variable, it is advisable to keep in mind the complexity, both temporally and spatially, of the chemistry in a system as large as the South Coast Air Basin (SoCAB).

2.3.3 Methodology

VOCs are not criteria pollutants and thus the amount of VOC data is much more limited than that for criteria pollutants such as NO_X and O_3. However, the recently implemented Photochemical Assessment Monitoring Stations (PAMS) program requires detailed VOC measurements at a number of sites in the SoCAB. For the PAMS program, several three hour-canister samples are collected every third day during July through September. The samples are analyzed for 56 C_2 – C_{11} target hydrocarbons (see Table 2.3-1) by a gas chromatograph equipped with a flame ionization detector. This method is not suitable for carbonyls such as formaldehyde and acetaldehyde and a separate analysis is performed for carbonyls. The VOC concentrations used in this analysis do not include carbonyls. In addition to the individual concentrations of the specific PAMS hydrocarbons, the analysis reports total non-methane organic compounds (TNMOC) which includes other non-identified or non-PAMS compounds. While some studies have indicated that the PAMS measurements underestimate the total hydrocarbon concentrations in the atmosphere by approximately 30% (Paulson, 1999), the PAMS data comprise the largest database of ambient hydrocarbon concentrations. For this reason, TNMOC from the PAMS program was used to estimate the VOC concentration in this study.

Sites in the SoCAB for which VOC data are available include Azusa, Banning, Burbank, Hawthorne, Los Angeles-North Main and Upland. While VOC data are available for a site in Pico Rivera, the data are suspect due to likely contamination from a neighboring facility and therefore were not used. VOC data for 1995 – 1998 were downloaded from EPA's AIRS database. Burbank and Hawthorne did not have VOC data for 1995 and 1996 and no TNMOC data for 1996 were available for Upland. Except for the Los Angeles-North Main site, in 1996 – 1998 3-hour canister samples were collected every third day starting at 23:00, 2:00, 5:00, 8:00, 11:00, 14:00, 17:00, and 20:00 PST. In 1995, the start time for the sampling was one hour later. Throughout 1995 – 1998, 2 three-hour samples were collected at 5:00 and 12:00 PST at the Los Angeles-North Main station. The program VOCDAT (Sonoma Technology, Inc., 1999) was used to generate files containing date, time, TNMOC, and Sum of PAMS Compounds. The Sum of PAMS Compounds as a percent of the TNMOC was calculated as a check for suspect data. Data were rejected if the Sum of PAMS Compounds was significantly greater than the TNMOC or if the Sum of PAMS Compounds represented less than 50% of the TNMOC.

Hourly average NO_X concentrations in ppm were obtained from ARB's ADAM database. The data were reported with 3 significant figures, except at Banning which reported NO_X concentrations with 2 significant figures. No quality control checks were performed. To allow comparison with 3-hour canister VOC samples, an average NO_X concentration was calculated by averaging the three hourly averages. Due to daily calibration checks, NO_X data are generally not available for 4:00 - 5:00 PST. Thus, the "3-hour" average NO_X concentrations for the periods beginning at 2:00 and 3:00 are averages of 2:00 to 4:00 and 3:00 to 4:00 and 5:00 to 6:00, respectively. The data were divided into weekday (Monday – Friday) and weekend (Saturday – Sunday) data sets. For each date and time, the ratio of Total NMOC in ppbC to NO_X in ppb was calculated. The arithmetic mean, standard deviation and standard error of the ratios were calculated.

2.3.4 Results

Figure 2.3-2 through Figure 2.3-6 show the VOC/NO_X values available for 1995 – 1998 for the five sites. The weekend data are offset by 15 minutes to display in the figures. Most of the data sets show occasional high values; however, the majority of the ratios are between 4 and 10. This supports a description of the chemistry of the region as likely being VOC-limited. Banning, a downwind site located on the eastern edge of the basin has the lowest ratios with the average ratio close to 3. Banning's VOC concentrations were significantly lower than the other sites, with TMNOC regularly less than 100 ppbC. The average VOC/NO_X as a function of time of day is shown in Figure 2.3-7 through Figure 2.3-11. The error bars represent one standard error. The average ratio, standard deviation, and n are given in Table 2.3-2 – Table 2.3-7. The weekend ratio is slightly higher than the weekday ratio during the morning at all sites. This increase in weekend ratio continues throughout the day, except at Azusa and Banning where the afternoon weekday ratio is slightly higher than the weekend. The percent increase of the average weekend VOC/NO_X over the average weekday VOC/NO_X is shown for all sites in Figure 2.3-12. (The 20:00 data for Banning are not shown.) The weekend morning ratios, between 5:00 and 11:00, are typically 10 to 30% higher than weekday ratios.

This finding of higher VOC/NO_X ratios on weekends was also observed by ENVIRON (ENVIRON, 1998). For the period 1994 – 1996, ENVIRON calculated an average weekday morning VOC/NO_X ratio of approximately 9 and a weekend ratio of approximately 14 at Los Angeles-North Main. While data collected at Azusa indicated slightly lower ratios of 6 and 9 for the weekday and weekend respectively, a similar increase of approximately 50% was observed in the weekend VOC/NO_X ratio. Thus, while both this analysis and ENVIRON's observed higher ratios on the weekend, the ARB analysis observed both lower absolute values for the VOC/NO_X ratios and a smaller percent increase on the weekend.

Although changes in gasoline occurred in the SoCAB in 1995, a more likely source of the discrepancy is the use of hydrocarbon data collected by different methods. Much of the VOC data used in the ENVIRON analysis was collected by Bendix 8202 continuous Total Hydrocarbon (THC) analyzers. The difference between the two analyses in observed increase in weekend VOC/NO_X ratios appears to be due to the smaller decrease observed for weekend VOC data. ENVIRON observed a 20% and 10% difference in weekend versus weekday THC in 1986-1989 and 1994-1996 respectively. TNMOC from the PAMS data, as seen in Table 2.3-7 and Figure 2.3-13, appears to show weekday VOC concentrations that are 20 to 50% higher than the weekend VOC concentrations.

Additional evidence that THC measurements exhibit a smaller decrease than VOC measurements do from weekday to weekend was noted by Leon Dolislager. He observed a significant difference in weekday to weekend VOC/NO_X ratios in data collected by the ARB in the 1980s (Dolislager, 2000). These ratios were also calculated using THC data and the increase in VOC/NO_X ratio was driven by the decrease in weekend NO_X because weekend THC declined only slightly on the weekend, with the weekend THC equal to approximately 90% of the weekday THC. If all of these observations are accurate, it implies there is a difference in the VOC inventory such that on the weekend there is an increase in compounds not measured by the PAMS but which are measured by THC methods. This could be explained by the Increased Weekend Emissions hypothesis. Professor Paulson at UCLA has developed an instrument that collects simultaneous measurements of TNMOC and

PAMS speciated data. Her results (Paulson, 1999) indicate that PAMS data underestimates hydrocarbon concentrations by approximately 30% overall. Examination of her ambient data may indicate if the ratio of PAMS hydrocarbons to TNMOC displays a weekend effect.

2.3.5 Conclusions

In general, VOC/NO_X ratios calculated using TNMOC from PAMS data range between 4 and 9, with weekend ratios 10 to 30% higher than weekday ratio at the same site and time. These numbers indicate that the ozone chemistry in the SoCAB is likely VOC limited and appears to support the NO_X-Reduction hypothesis. However, this conclusion should be regarded as tentative for a number of reasons. Actual hydrocarbon concentrations may be as much as 30% greater than those used in this analysis. This would result in VOC/NO_X ratios that are also 30% greater. Also, the difference in the relative weekday to weekend change in THC data versus PAMS data indicates there may be a difference in the VOC composition on the weekend versus the weekdays. If this were true is would support the Increased Weekend Emissions hypothesis. The composition of the mixture represented by NO_X also changes on the weekend. For example, section 5.1 found that NO_2/NO ratios are generally higher on early Sunday morning. Thus, it would be unwise to predict the effect of a 10 to 30% change in the VOC/NO_X without a more thorough understanding of the shapes of isopleths appropriate for each site and time.

2.3.6 Recommendations

1) PAMS data provides only 3-hour average VOC concentrations every third day. To more accurately characterize the diurnal variations in VOC/NO_X ratios, hourly total VOC measurements should be collected at ten sites in the SoCAB for at least 18 months. The study should include two ozone seasons to lessen the impact of unusual meteorology.

2) VOC concentrations estimated from PAMS data underestimate actual VOC concentrations. If the missing portion is assumed to be a fixed percentage, this underestimation would not change the percent change in weekend VOC/NO_X ratios but would increase the absolute VOC/NO_X ratio. For this reason VOC/NO_X should be recalculated to include carbonyls and/or an increase of approximately 30% in VOC concentrations.

3) An investigation of the possible differences in between THC and Total NMOC from the PAMS analysis should be undertaken as this may support the hypothesis that weekend emissions of VOC may be different in some way due to weekend activities.

2.3.7 References

ENVIRON International Corporation, (1998) “Analysis of Weekend-Weekday Differences in Ozone and Ozone Precursors in the South Coast (Los Angeles) Air Basin” Prepared for American Automobile Manufacturers Association.

Dolislager, Leon, personal communication (2000)

Finlayson-Pitts, B. J., J. N. Pitts, Jr, (2000) “Chemistry of the Upper and Lower Atmosphere”, Academic Press.

Paulson, S. (1999) “Total Non-Methane Organic Carbon Development and Validation of a New Instrument and Measurements of Total Non-Methane Organic Carbon and C2-C10 Hydrocarbons in the South Coast Air Basin”, ARB Contract No. 95-335.

Table 2.3-1. Hydrocarbon and carbonyl species measured in the Photochemical Assessment Monitoring Stations (PAMS) program. (Listed in elution sequence)

1	Ethylene	21	Ethylbenzene
2	2,3-dimethylpentane	22	1-Pentene
3	Acetylene	23	m&p-Xylenes
4	3-methylhexane	24	n-Pentane
5	Ethane	25	Styrene
6	2,2,4-trimethylpentane	26	Isoprene
7	Propylene	27	o-Xylene
8	n-Heptane	28	t-2-pentene
9	Propane	29	n-Nonane
10	Methylcyclohexane	30	c-2-pentene
11	Isobutane	31	Isopropylbenzene
12	2,3,4-trimethylpentane	32	2,2-Dimethylbutane
13	1-Butene	33	n-Propylbenzene
14	Toluene	34	Cyclopentane
15	n-Butane	35	m-Ethyltoluene
16	t-2-Butene	36	2,3-dimethylbutane
17	3-methylheptane	37	p-Ethyltoluene
18	c-2-Butene	38	2-methylpentane
19	n-Octane	39	1,3,5-Trimethylbenzene
20	Isopentane	40	3-Methylpentane

Table 2.3-1 (continued). Hydrocarbon and carbonyl species measured in the PAMS program. (Listed in elution sequence)

41	o-Ethyltoluene	51	p-Diethylbenzene
42	2-Methyl-1-Pentene	52	Cyclohexane
43	1,2,4-trimethylbenzene	53	n-Undecane
44	n-hexane	54	2-methylhexane
45	n-Decane	Carbonyls	
46	Methylcyclopentane		Formaldehyde
47	1,2,3-trimethylbenzene		Acetone
48	2,4-dimethylpentane		Acetaldehyde
49	m-Diethylbenzene		
50	Benzene		

Table 2.3-2. VOC/NO_X ratios at Azusa.

		Weekday			Weekend		
Year	**Time**	**Average**	**Stdev**	**N**	**Average**	**Stdev**	**N**
1995	0:00	6.4	2.1	15	6.4	1.0	7
1996-1998	2:00	6.9	2.4	51	8.2	2.9	21
1995	3:00	5.1	1.2	13	6.7	0.9	7
1996-1998	5:00	6.0	2.4	54	7.5	2.8	22
1995	6:00	4.5	0.9	14	4.4	1.5	7
1996-1998	8:00	5.4	2.2	55	6.6	2.3	22
1995	9:00	4.6	0.9	13	5.0	2.1	7
1996-1998	11:00	6.3	2.2	52	7.4	2.6	21
1995	12:00	5.8	1.6	14	6.3	2.0	7
1996-1998	14:00	6.5	2.7	54	7.0	1.9	18
1995	15:00	6.4	2.1	13	5.4	0.8	6
1996-1998	17:00	6.0	2.6	51	6.6	2.4	19
1995	18:00	5.6	1.3	14	5.2	0.7	6
1996-1998	20:00	5.9	2.6	52	5.9	2.1	20
1995	21:00	5.4	1.4	14	5.1	0.5	6
1996-1998	23:00	7.2	3.1	53	6.7	1.6	18

Table 2.3-3. VOC/NO_X ratios at Burbank based on data for 1998.
(plus 9 days in 1997)

	Weekday			Weekend		
Time	**Average**	**Stdev**	**N**	**Average**	**Stdev**	**N**
2:00	6.8	1.7	60	7.1	1.2	27
5:00	5.7	1.0	60	6.7	1.0	26
8:00	6.5	1.7	56	7.2	1.7	25
11:00	7.6	1.4	62	9.3	2.9	27
14:00	8.5	5.8	61	8.0	1.5	24
17:00	6.5	1.1	64	6.7	0.9	27
20:00	5.8	1.4	64	6.6	1.5	27
23:00	5.9	1.7	63	6.4	2.0	25

Table 2.3-4. VOC/NO_X ratios at Hawthorne based on data for 1997 and 1998.

	Weekday			Weekend		
Time	**Average**	**Stdev**	**N**	**Average**	**Stdev**	**N**
2:00	7.3	3.1	21	8.1	5.3	8
5:00	5.5	3.1	29	7.1	3.1	10
8:00	7.3	2.1	24	9.3	5.7	10
11:00	8.7	3.6	21	10.6	3.2	10
14:00	6.3	3.3	17	7.5	3.0	7
17:00	9.2	9.6	15	9.3	6.8	5
20:00	7.1	4.0	12	5.8	1.8	4
23:00	6.2	2.0	19	8.6	4.4	6

Table 2.3-5. VOC/NO_X ratios at L.A. – N. Main based on data for 1995 – 1998.

	Weekday			Weekend		
Time	**Average**	**Stdev**	**N**	**Average**	**Stdev**	**N**
5:00	3.6	1.3	64	4.8	1.3	26
12:00	6.9	3.0	66	7.6	2.9	25

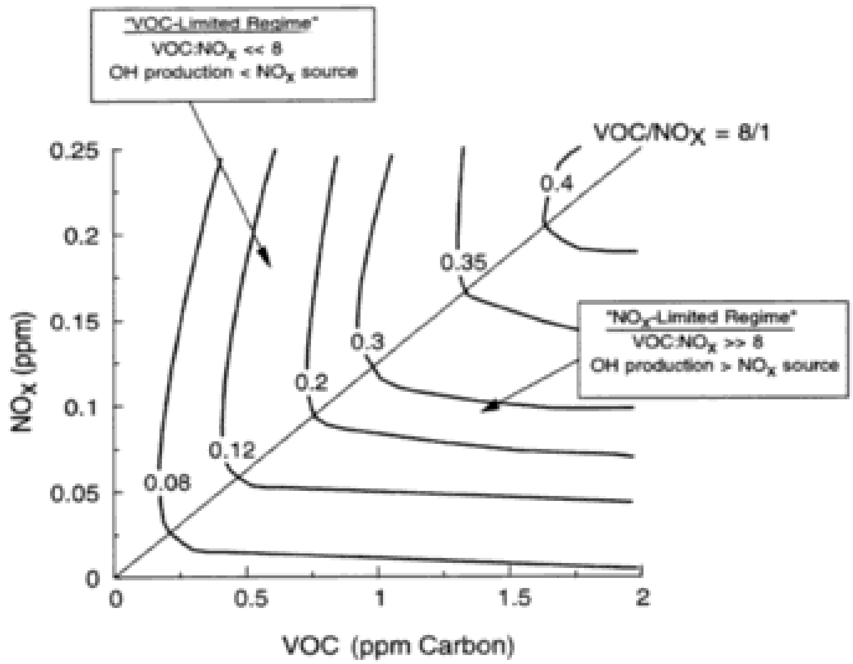
Table 2.3-6. VOC/NO_X ratios at Upland based on data for 1995, 1997, and 1998.

		Weekday			Weekend		
Year	**Time**	**Average**	**Stdev**	**N**	**Average**	**Stdev**	**N**
1995	0:00	8.3	2.7	15	7.9	1.7	9
1996-1998	2:00	8.2	2.7	42	7.8	3.3	12
1995	3:00	5.9	2.6	15	7.7	1.8	9
1996-1998	5:00	4.6	1.2	40	7.1	2.1	12
1995	6:00	4.4	0.9	15	5.1	0.9	9
1996-1998	8:00	4.4	1.2	43	5.7	2.2	11
1995	9:00	4.0	1.0	15	5.4	2.2	9
1996-1998	11:00	5.0	1.9	36	6.3	2.2	12
1995	12:00	4.2	1.5	13	4.8	0.8	8
1996-1998	14:00	5.2	1.3	40	7.1	2.9	10
1995	15:00	3.6	1.0	15	5.0	1.6	7
1996-1998	17:00	5.2	2.4	43	5.3	2.4	10
1995	18:00	4.8	1.6	14	5.5	1.3	7
1996-1998	20:00	5.2	1.5	39	5.9	2.6	12
1995	21:00	6.0	1.6	14	7.0	0.7	7
1996-1998	23:00	7.0	1.8	34	7.7	2.2	14

Table 2.3-7. Ratio of average weekday TNMOC to average weekend TNMOC.

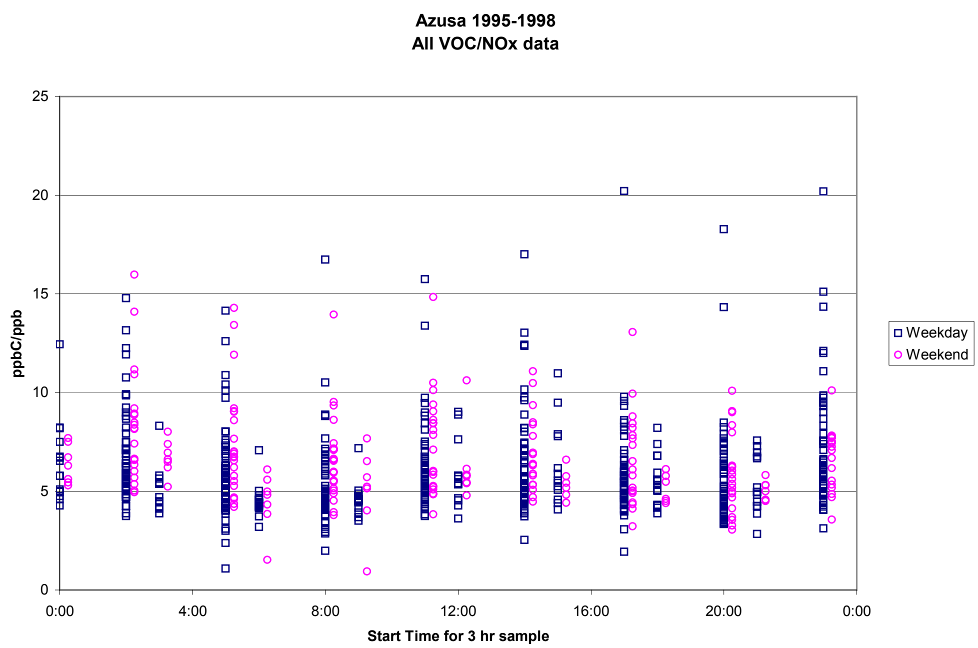
Time	Azusa	Banning	Burbank	Hawthorne	North Main	Upland
5:00	1.3	1.5	1.1	1.3	1.3	1.5
6:00	1.5					1.4
8:00	1.4	1.1	1.3	1.0		1.4
9:00	1.4					1.1
11:00	1.4	2.0	1.2	1.1		1.4
12:00	1.4				1.2	1.3

Figure 2.3-1. Schematic EKMA diagram illustrating the relationship between the concentrations of VOC and NO_X and the resulting maximum ozone concentration (parts per million).



Source: National Research Council (1999) *Ozone-Forming Potential of Reformulated Gasoline,* National Academy Press, Washington, DC.

Figure 2.3-2.



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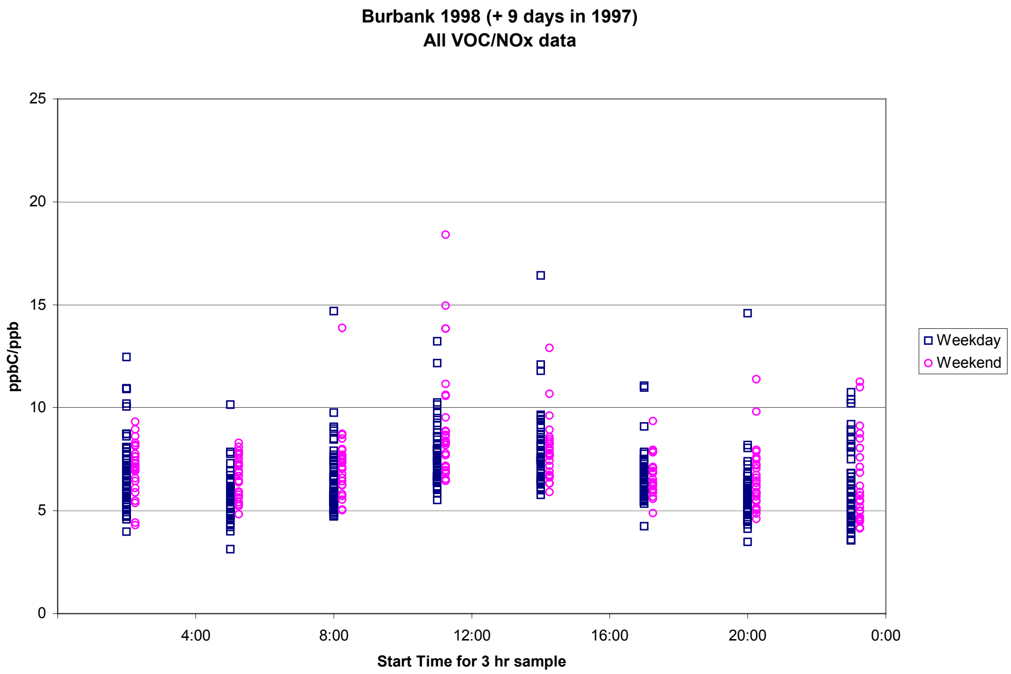

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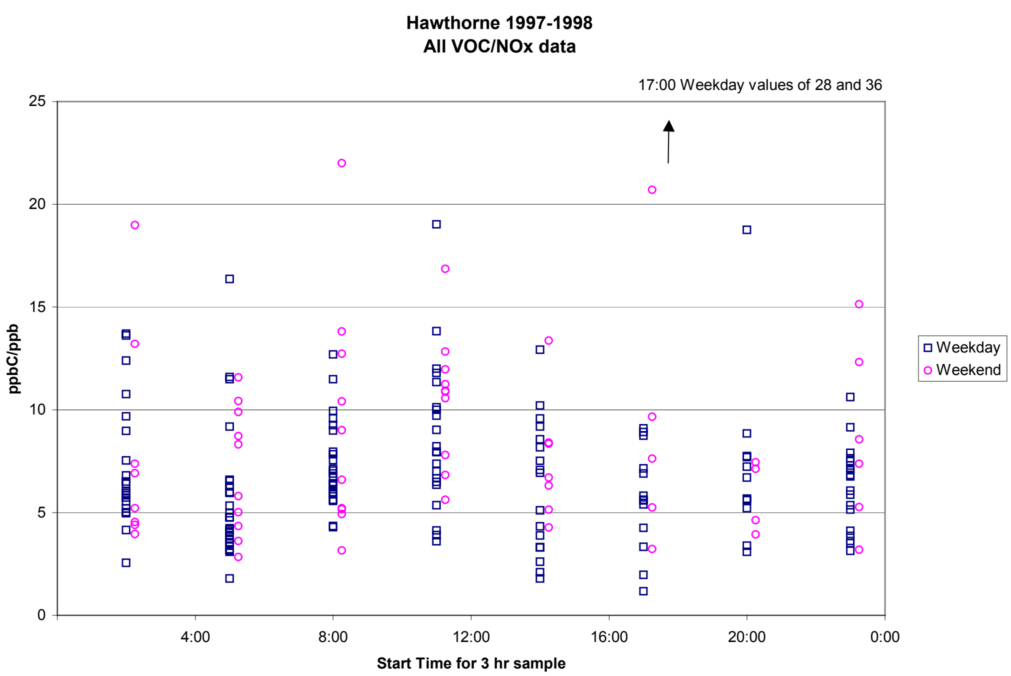

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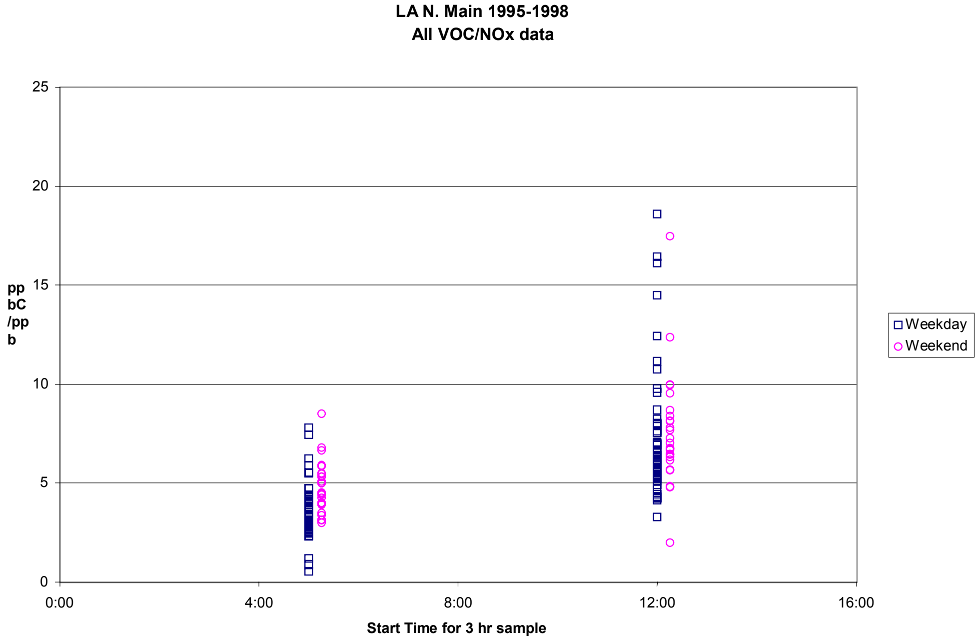

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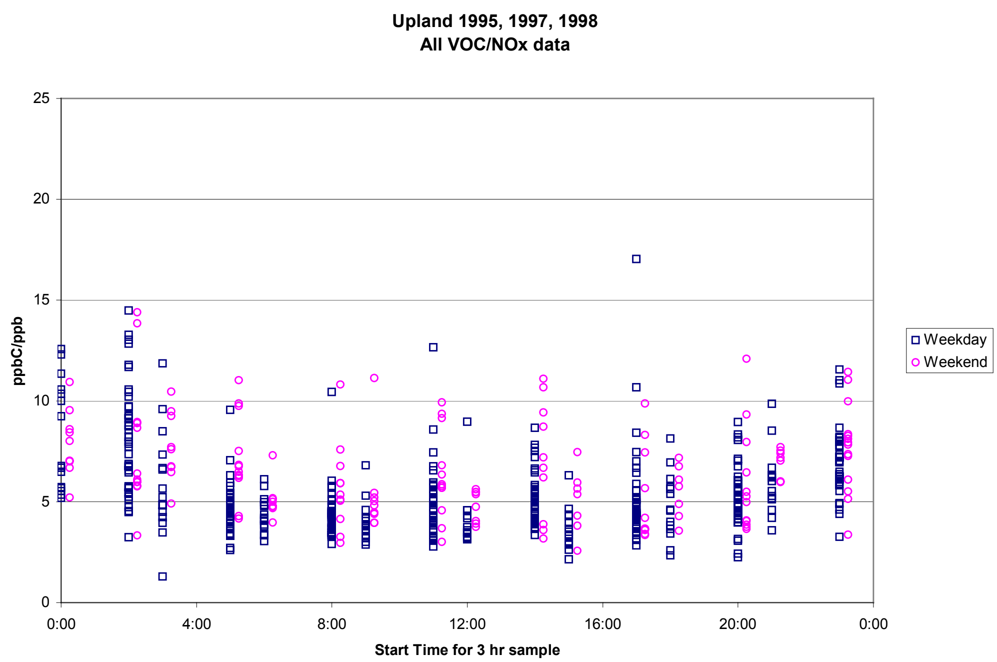

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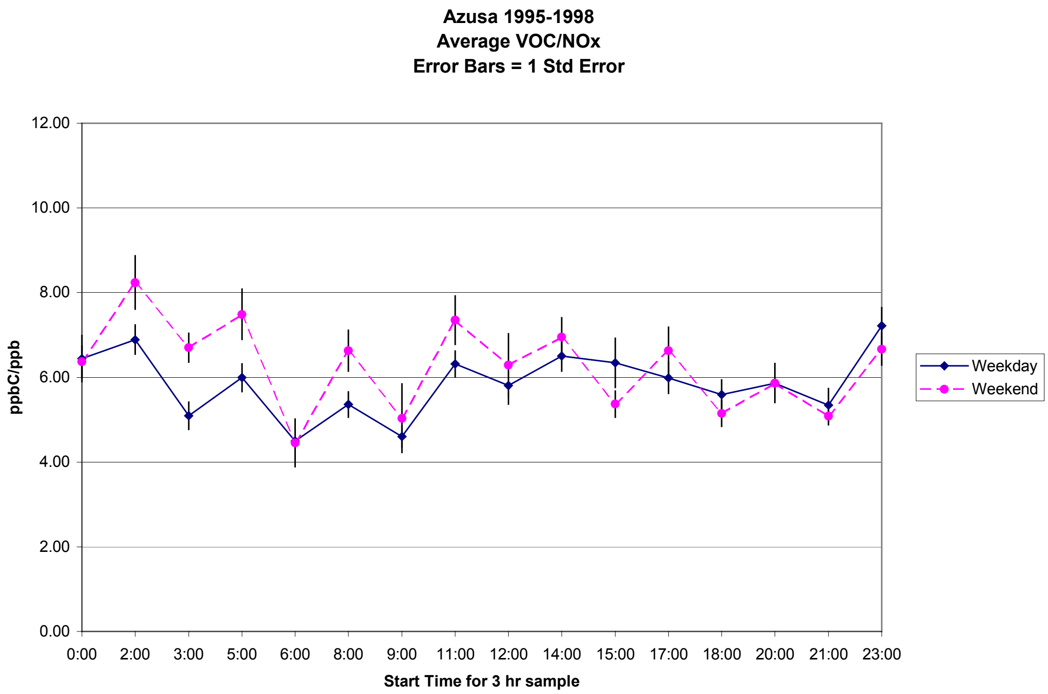

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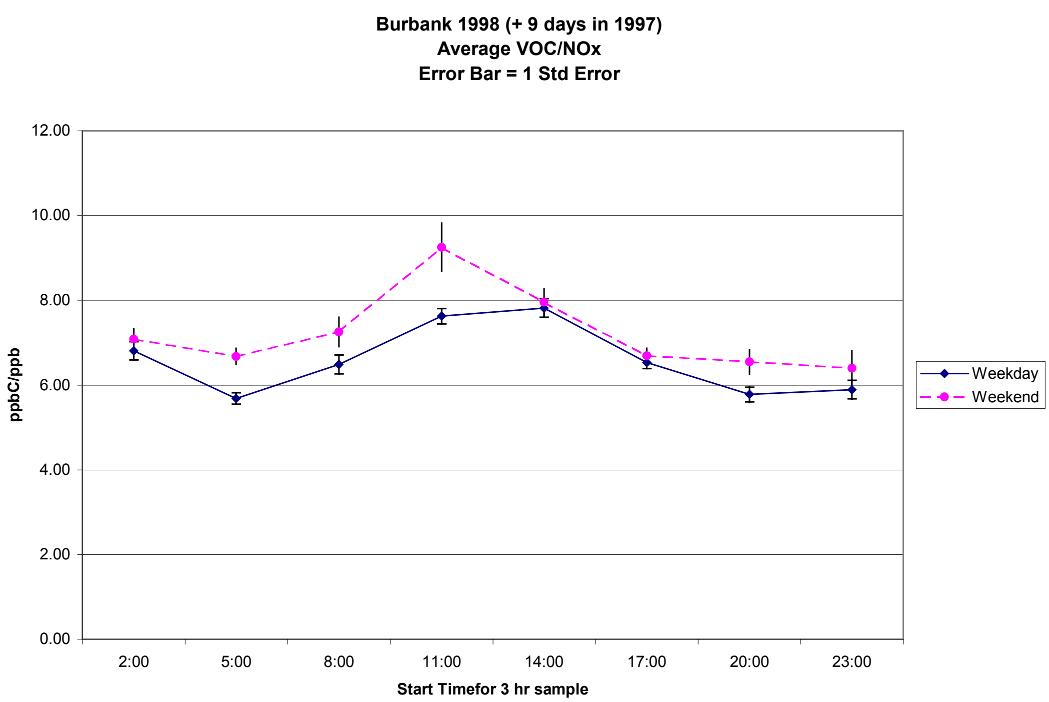

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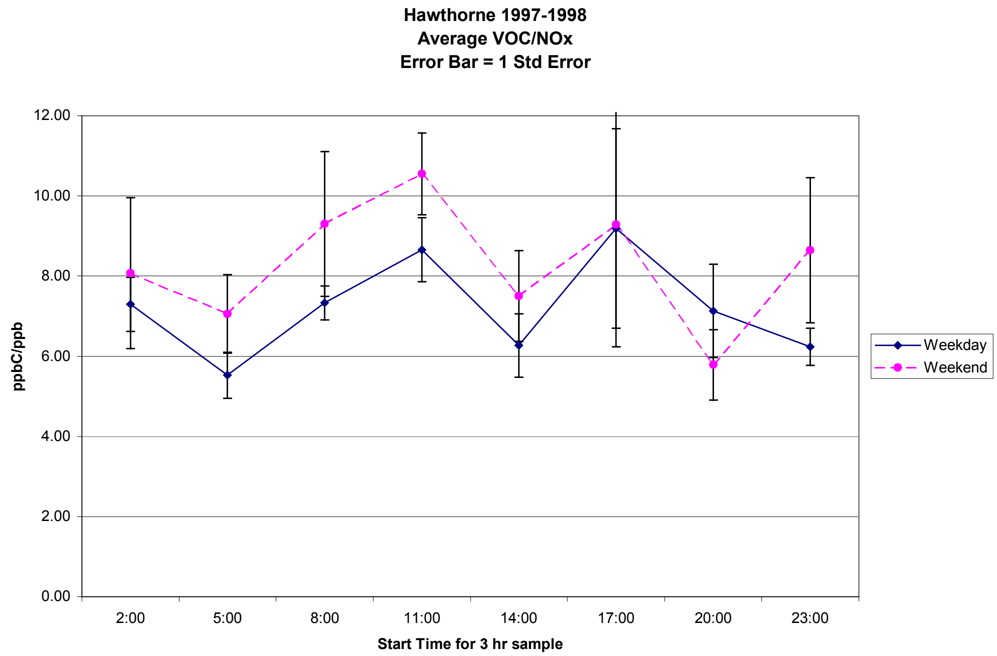

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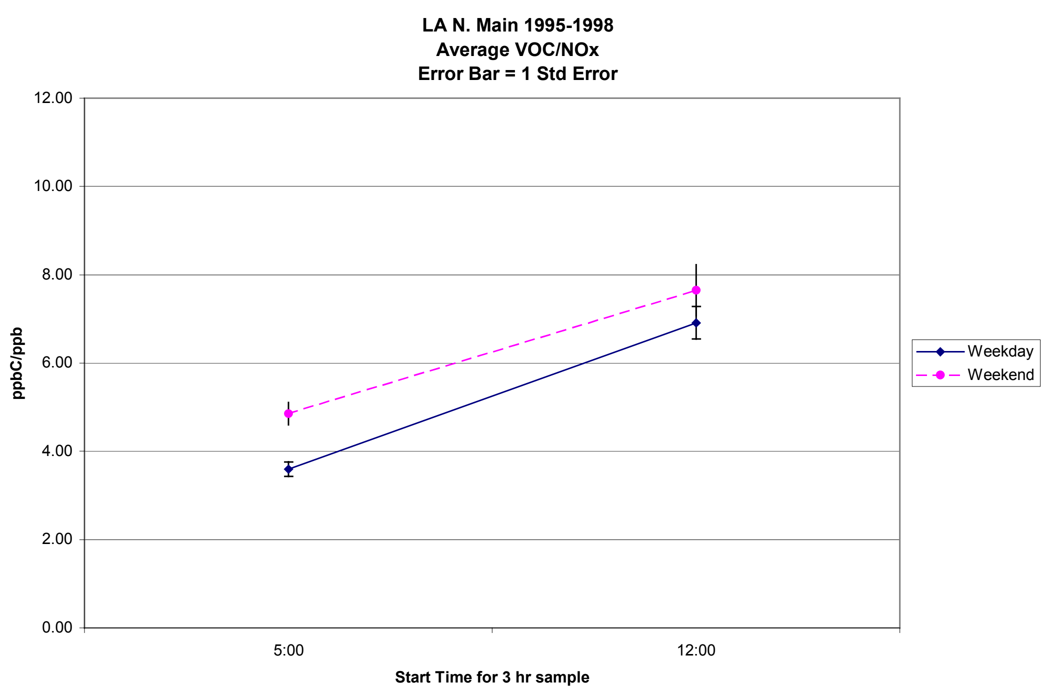

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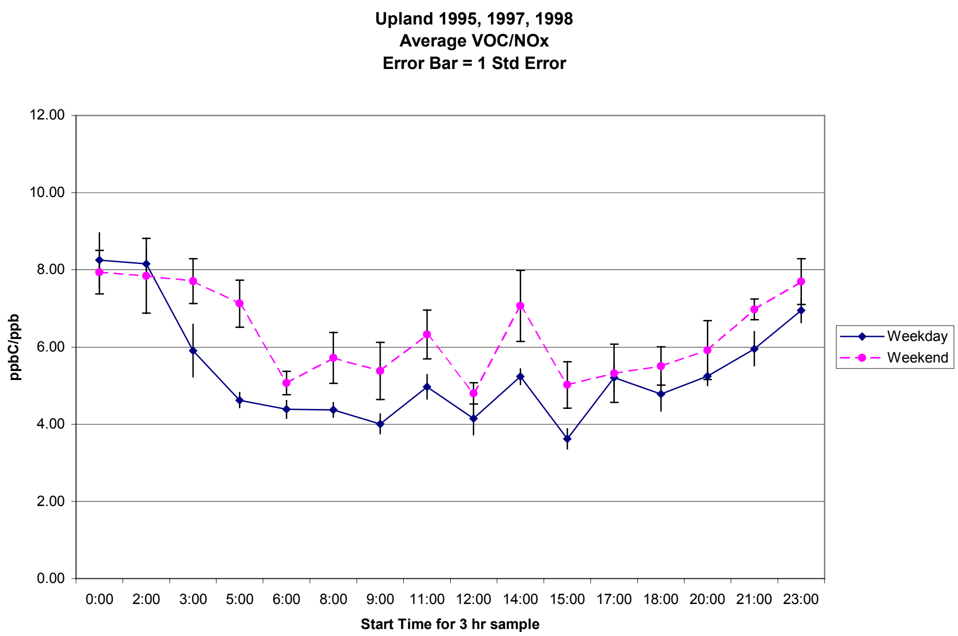

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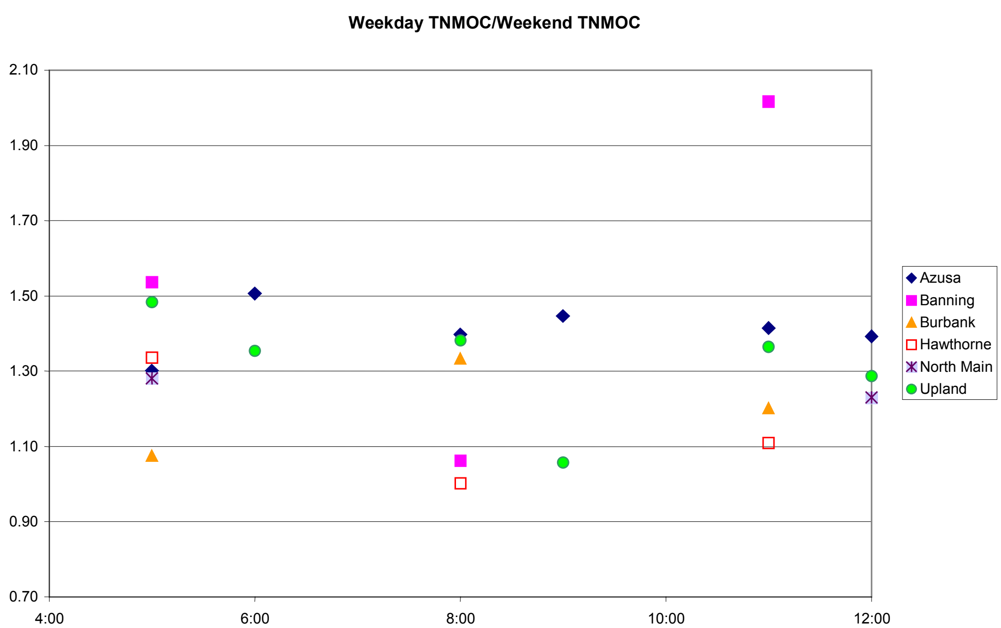

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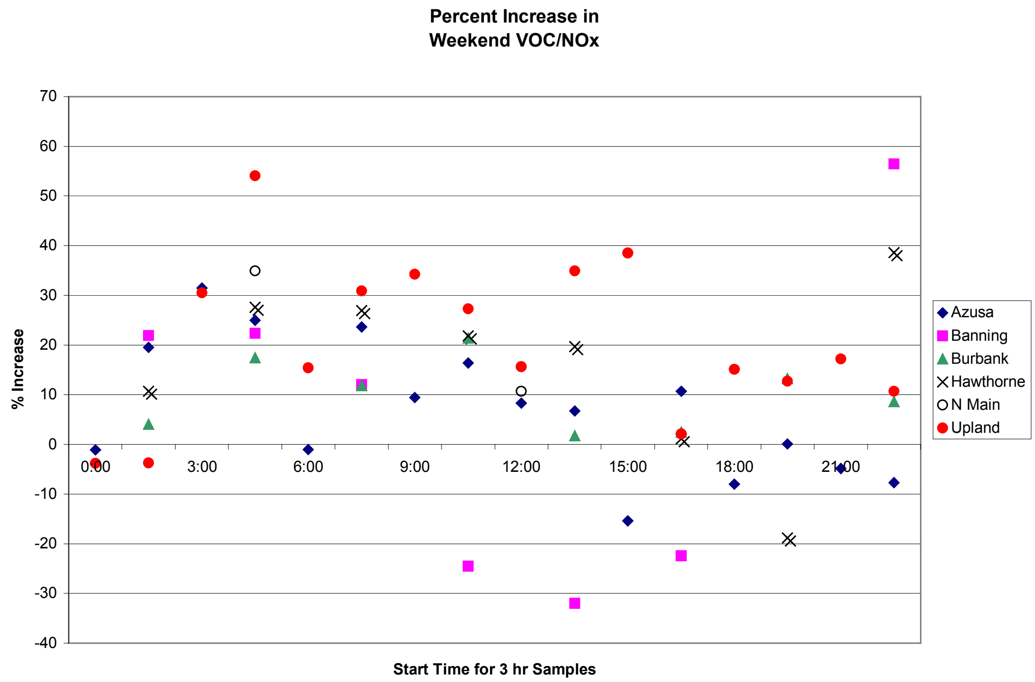

Percent Increase in
Weekend VOC/NOx
70
60
50
40
30
20
10
0
-10
-20
-30
-40
% Increase
0:00
3:00
6:00
9:00
12:00
15:00
18:00
21:00
Start Time for 3 hr Samples
Azusa
Banning
Burbank
Hawthorne
N Main
Upland

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